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Preparation and characterization of W/γ-Al$_2$O$_3$ and Pd–W/γ-Al$_2$O$_3$ catalysts from organometallic precursors. The catalytic activity for NO decomposition

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Abstract

The photochemical reaction of W(CO)$_6$ with triphenylphosphine (PPh$_3$) in the presence of γ-Al$_2$O$_3$ and Pd/γ-Al$_2$O$_3$ has been used to prepare W/γ-Al$_2$O$_3$ and Pd–W/γ-Al$_2$O$_3$ catalysts. Adsorbed mono- and disubstituted W species have been identified by FTIR spectroscopy. There is evidence of the adsorption of W(CO)$_{6-x}$L$_x$ species on both the alumina and the Pd surface. After thermal decomposition and reduction at 573 K the catalysts have been characterized by FTIR spectroscopy of adsorbed NH$_3$, CO and NO. The retention of W and P suppresses the Lewis acidity of the alumina support. On Pd–W/γ-Al$_2$O$_3$, the W is present in a partially reduced state in close association with Pd. This interaction modifies the chemisorptive properties of NO relative to those of the monometallic Pd and W catalysts. In line with these observations the Pd–W/γ-Al$_2$O$_3$ catalyst presents an enhanced activity for NO decomposition at 473 K. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Metal carbonyls; Alumina; Surface species; Characterization; NO decomposition

1. Introduction

Recently there has been a growing interest in the use of Pd as the only active metal for exhaust catalysts, due to its low cost as compared with Pt and Rh. Previous studies have shown that Pd can catalyze the reduction of nitric oxide [1] to N$_2$ in addition to its well known activity for hydrocarbons and carbon monoxide oxidation. However in the presence of hydrocarbons the nitric oxide removal capacity of Pd under reducing conditions is inferior to that of Rh containing catalysts [2]. In order to overcome this limitation, palladium catalysts promoted with metal oxides such as MnO$_x$, MoO$_3$ and WO$_3$ have been proposed [3–5]. In principle W, in the reduced state, is quite active for NO decomposition [6], but it is difficult to obtain cations in a low oxidation state when the metal is well-dispersed and isolated on the alumina surface. However it is expected that the close proximity of Pd and W may facilitate the partial reduction of WO$_3$. Using inorganic precursors, catalysts with adequate metal–metal contact could be prepared but it requires the use of high metal loadings. Consequently W and

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Mo volatilization occur under oxidizing conditions [7]. A better approach to prepare Pd–W catalysts may be the use of organometallic precursors. It is known that they allow the preparation of well-dispersed, low valence species without high thermal treatments. Using $[W(CO)_6]$, Kazusaka and Howe [8] prepared W on alumina catalysts, but the maximum metal loading was about 0.3%. Upon activation at 200°C and adsorption of NO they were able to observe a pair of IR bands assigned to $W^{+4} (NO)_2$ species. An improved procedure to deposit W, Mo and Cr on alumina has been recently introduced [9] and is based on the photochemical reaction of $[M(CO)_6]$ (M = Cr, Mo, W) with PPh_3. The substitution of CO in $W(CO)_6$ for PPh_3 ligands allows the formation of mono- and disubstituted species that interact more strongly with the alumina support than pure hexacarbonyls. Moreover the irradiation time could be used as a preparation variable to adjust the metal loading. As mentioned before, our aim is to stabilize reduced W on the Pd particles, to observe the effect of the second metal on the activity of Pd for NO decomposition. We expect that a good Pd–W interaction may develop either during the W adsorption process or following the removal of the ligands. In this work the surface species formed on $Pd/\gamma-Al_2O_3$ by the photochemical reaction of $[W(CO)_6]$ with PPh_3 have been identified by FTIR and ^{13}C NMR analysis and compared with those present on the pure support. Upon thermal treatment to decompose the substituted carbonyls the resulting mono and bimetallic catalysts have been characterized by the FTIR spectra of adsorbed NH_3, CO and NO. Finally the NO decomposition reaction has been used to investigate the influence of W on the catalytic activity of Pd.

2. Experimental

The palladium on alumina catalyst was prepared by the wet impregnation technique using a benzene solution of palladium acetylacetonate and $\gamma-Al_2O_3$ (Rhone-Poulenc, 206 m^2/g). The solid and the solution were left in contact for 24 h at room temperature. After impregnation the liquid was removed and the solid dried in N_2. Subsequently the solution was calcined in air at 573 K for 2 h and then reduced in flowing hydrogen at the same temperature. Using this palladium catalyst and the pure alumina support, $Pd–W/\gamma-Al_2O_3$ and $W/\gamma-Al_2O_3$ catalysts were obtained. In order to carry out the photochemical reaction between $[W(CO)_6]$ and PPh_3 under inert atmosphere the Schlenk technique was used. The $\gamma-Al_2O_3$ was first evacuated at 723 K for 1 h and then cooled in Ar. For the $Pd/\gamma-Al_2O_3$ catalyst a 1 h hydrogen treatment at 573 K was performed before cooling to room temperature. In a typical experiment, 1 g of solid was added to a pentane solution of $W(CO)_6$ (40 cm^3, 6.7% M) and mixed continuously for 30 min. The amount of W added was enough to obtain a 5 wt.% loading and the $[W(CO)_6]$ to PPh_3 molar ratio was 1/2. The photochemical reactions were performed in an Ar atmosphere using a Philips HPL-N (125 W) UV lamp fitted into a Pyrex cold finger. The transmitted UV wavelength was limited by the Pyrex glass to 220 nm. In accordance with previous studies [9] the slurry was irradiated during 6 h to ensure a maximum loading of W. In order to observe the reaction progress small liquid samples were withdrawn to be analyzed by FTIR. After reaction the liquid solution was removed, the solid washed several times with pentane, evacuated for 1 h and finally stored under Ar. The contents of Pd, W and P were determined by AAS (Pd and W) and ICP (P).

Adsorbed species on the catalyst precursors were identified by FTIR spectroscopy. Infrared experiments were performed in a Nicolet 20 DXB instrument at 4 cm^{-1} resolution. Catalyst samples of approximately 30 mg were pressed to form transparent disks of 10 mm in diameter that were mounted in a heated metal holder. The holder was placed in the beam path of a stainless steel cell sealed with CaF_2 windows, and coupled to a vacuum system for evacuation to

10^{-6} Torr. It was possible to perform heat treatments up to 573 K, to dose small amounts of CO, NO and NH_3 through a leak valve or maintain a steady flow of H_2 or He. A MKS Baratron Type 170 M allows pressure measurements in the 0.1–10 Torr range.

The FTIR characterization of the Pd–W/γ-Al_2O_3 and W/γ-Al_2O_3 catalysts precursors was first performed on samples evacuated at room temperature (an empty cell was used as a background). Subsequently the samples were heated in He up to 573 K to decompose the tungsten carbonyls; a FTIR spectrum was taken under this condition to verify the absence of surface species. After reduction in flowing hydrogen at the same temperature the samples were cooled in flowing He to room temperature. An evacuated background spectrum was then taken for adsorption studies. In typical experiments adsorbates (CO, NO and NH_3) were dosed at pressures of 1 to 5 Torr and the samples exposed to the gas phase for 2 to 5 min prior to spectra measurement. Scanning time was about 1 min. Finally the cell was evacuated to 10^{-5} Torr for 2 min and a new spectrum was taken. Gas pressures, contact time and temperatures were well-controlled in order to facilitate the comparison of results for different samples.

The ^{13}C-NMR spectrum of the species extracted from the alumina surface with CH_2Cl_2 was obtained in $CDCl_3$ solution on a Varian Gemini VXR 200 MHz instrument and externally referred to TMS. The spectrum was recorded after 20 000 scans at room temperature with a pulse width of 45° and pulse delay of 1.5 s. The relaxing agent $[Cr(acac)_3]$ was added to overcome the long T_1 relaxation time of the carbonyl resonance.

Catalytic experiments were carried out in a flow reactor mounted in an electric furnace. Samples of 0.1 g were packed in a 1/4 in. SS tube with a thermocouple placed at the reactor entrance. The NO decomposition reaction was studied as a function of time at 473 K and 573 K, using a feed mixture containing 340 ppm of NO in a He background (Matheson, certified).

The flow rate was adjusted at 30 cm^3/min. Prior to reaction the catalysts were reduced in situ at 473 K. Gas chromatographic separation of reactant and products was achieved by means of two Porapak Q columns. One (1/8 in. × 6 mts) was operated at 263 K for the separation of NO and N_2; another (1/8 in. × 2.4 mts) at 313 K allowed the identification of N_2O.

3. Results and discussion

3.1. Identification of adsorbed carbonyls on γ-Al_2O_3 and Pd / γ-Al_2O_3

FTIR analysis of solid samples washed with pentane have shown that fairly stable adsorbed species remained on the surface. Strong bands in the 1800–1950 cm^{-1} region, corresponding to monosubstituted and disubstituted carbonyls, was the relevant feature observed on γ-Al_2O_3. This situation is clearly observed in Fig. 1. A small amount of $[W(CO)_6]$ remains on Al_2O_3 after washing, as seen by the band located at 1985 cm^{-1} (T_{1u} mode, O_h symmetry). Bands that appear at 1946 cm^{-1} ($A_1^{ax} + E$) and 2072 cm^{-1} (A_1^{rad}) are due to monosubstituted
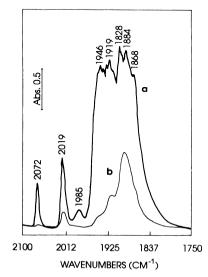

Fig. 1. FTIR Spectra of adsorbed carbonyl species on γ-Al_2O_3 (a) and Pd/γ-Al_2O_3 (b).

[W(CO)$_5$L] species. On the other hand the bands located at 1868, 1884, 1898, 1919 and 2019 cm^{-1} correspond to [W(CO)$_4$L$_2$] species. Either the band at 1884 cm^{-1} or the one at 1898 cm^{-1} is due to *trans*- [W(CO)$_6$L$_2$] (E$_u$ mode, D$_{4h}$ symmetry). The other four bands correspond to A$_1$, A$_1$, B$_1$ and B$_2$ modes of *cis*-[W(CO)$_4$L$_2$] (C$_{2v}$), going from low to high wavenumbers. The *trans* species are occluded by the more abundant *cis* species. Consequently a NMR analysis was performed for the species extracted from the W/γ-Al$_2$O$_3$ sample. The NMR spectrum of the tungsten carbonyl compounds showed bands related to [W(CO)$_6$] (191.1 ppm), [W(CO)$_5$ PPh$_3$] (doublet at 197.2 ppm, $J_c - P = 6.9$ Hz due to the carbonyls *cis* to the phosphine ligand), *cis*-[W(CO)$_4$ (PPh$_3$)$_2$] (two triplets, one at 205.4 ppm, $J_c - P = 9.6$ Hz related to the CO's *trans* to the ligand and the other at 203.6 ppm, $J_c - P = 7.3$ Hz due to the CO's *cis* to the phosphines). The higher intensity of the triplet at 203.6 ppm is supposed to be due to the presence of *trans*-[W(CO)$_2$ (PPh$_3$)$_2$]. The band integration showed a *trans* to *cis* ratio of 0.4, confirming the predominance of *cis* species.

It is well-known that metal carbonyls become attached to Al^{+3} Lewis acid sites through the oxygen atom in the CO ligands [10]. When these ligands are replaced by PPh$_3$, the electron density in the metal increases and consequently the species coordinated to surface sites are more stable. An interesting experimental observation is that only monosubstituted species were detected in solution. Apparently the adsorption of monosubstituted carbonyls facilitates the elimination of CO ligands not involved in bonding, which in turn may be replaced by PPh$_3$ ligands to form the disubstituted species. The 2.2% W loading on γ-Al$_2$O$_3$, shown in Table 1, indicates that PPh$_3$ ligands facilitate the attachment of carbonyls to the support surface. It is relevant to recall that a maximum W loading of about 0.3% was obtained by Kazusaka and Howe [8] when the hexacarbonyl was adsorbed from the vapor phase, although the values cannot be

Table 1
Composition of catalysts precursors prior to thermal treatments

	Pd (wt.%)	W (wt.%)	P (wt.%)
γ-Al$_2$O$_3$[a]	–	–	0.48 (0.27)[b]
W/γ-Al$_2$O$_3$	–	2.2	0.54
Pd–W/γ-Al$_2$O$_3$	0.78	1.8	0.21

[a] PPh$_3$ adsorption in the absence of W(CO)$_6$.
[b] Numbers in parentheses give the P content after the He and H$_2$ treatments.

strictly compared due to differences in the support area.

The Lewis acid sites on the alumina surface may also be occupied by PPh$_3$, taking into account that it is a strong base. In other words we cannot exclude a competition of PPh$_3$ and substituted carbonyls for the adsorption sites. A clear FTIR evidence of PPh$_3$ adsorption on γ-Al$_2$O$_3$ was found when the photochemical reaction was carried out in the absence of W(CO)$_6$; an intense band was present at 1438 cm^{-1}. The subsequent ICP analysis confirmed the presence of 0.48% by weight of P (see Table 1). In the presence of W(CO)$_6$, the P uptake of γ-Al$_2$O$_3$ was slightly higher; 0.54%. Consequently the P content arises mainly from adsorption of PPh$_3$ on the support surface although the ligands from mono and disubstituted tungsten carbonyls may become an additional source of P.

The spectra of adsorbed species was quite different on Pd/γ-Al$_2$O$_3$. As seen in Fig. 1 the bands were less intense, and mainly due to disubstituted species that seems to be more stable. Therefore the amount of W expected was less than that on γ-Al$_2$O$_3$. However the values in Table 1 in fact indicate that the W loading was slightly lower, 1.8%, while the major difference was in the amount of P; it decreased from 0.54% to 0.21%.

The appreciable decrease of intensity in the FTIR spectra of adsorbed carbonyls and the reduced P uptake on Pd/γ-Al$_2$O$_3$, relative to those on γ-Al$_2$O$_3$, may imply that the presence of Pd limits the sites where attachments of substituted metal carbonyls and PPh$_3$ take place.

Information about the relative concentration and strength of Lewis acid sites was obtained by inspection of the spectra of adsorbed NH_3.

As seen in Fig. 2, the presence of Pd slightly alters the band due to the symmetric deformation vibration of NH_3 adsorbed on γ-Al_2O_3; on Pd/γ-Al_2O_3 the band at 1267 cm^{-1} [11], is broader. On the basis of this result a diminished interaction of PPh_3 and carbonyl species with the Lewis acid sites of Pd/γ-Al_2O_3, relative to those on γ-Al_2O_3, should not be expected. Consequently the large decrease in intensity of adsorbed carbonyls, the slight variation in the W content and the decrease in P content are difficult to explain. Our interpretation is based on the assumption that substituted carbonyls interact with both the alumina support and the Pd surface. In addition we suspect that [W-$(CO)_{6-x}L_x$] species adsorbed on the metal lose the ligands during the long irradiation time and consequently only a fraction of the attached W contribute to the adsorption spectra. This is in accordance with a lower P content on Pd–W/γ-Al_2O_3. Supporting this interpretation we
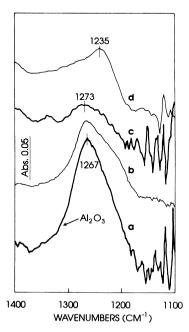

Fig. 2. FTIR Spectra of NH_3 adsorbed on γ-Al_2O_3 (a), Pd/γ-Al_2O_3 (b), Pd–W/γ-Al_2O_3 (c) and W/γ-Al_2O_3 (d).

have observed that catalyst samples examined after a reaction time of 2 h, showed more intense IR bands than those in Fig. 1. We recognize that additional studies are needed to describe the palladium–hexacarbonyl interaction in more detail. No information has been found on the reactivity of supported group-VIII metals with hexacarbonyls compounds.

Following the addition of W significant alterations were observed on the spectra of adsorbed NH_3. It is seen in Fig. 2, that on W/γ-Al_2O_3 the characteristic band experiences a marked decrease in intensity and it is shifted to a lower IR frequency (1234 cm^{-1}), an indication that only weak Lewis acid sites remain on the surface. This behavior is due to W and P content interacting with exposed Al^{3+} sites. Moreover, as Bronsted acid sites are not formed it is reasonable to conclude that the elements remain in a low valence state. On Pd/γ-Al_2O_3 the addition of W and P also reduced the concentration of acid sites but the frequency maintained its value (1273 cm^{-1}). These results are in line with a lower amount of W and P on the Al_2O_3 surface. Regarding the effect of P, it is important to state that the contents given in Table 1 have been determined prior to thermal treatments in He and H_2. The elimination of PPh_3 occurs during the hydrogen activation step at 573 K, leading to lower levels of P on the reduced samples. This behaviour was verified when γ-Al_2O_3 exposed to PPh_3 was heated in He and H_2. The P content decrease from 0.48% to 0.27% (Table 1) and the PPh_3 band at 1438 cm^{-1} was strongly attenuated. In the presence of Pd the elimination of PPh_3 should be more effective [12].

3.2. Adsorption of CO and NO

After a heat treatment in He at 573 K, a spectra ratioed with the initial empty cell background indicated the absence of residual carbonyl species on both, W/γ-Al_2O_3 and Pd–W/γ-Al_2O_3. These samples and that of Pd/γ-Al_2O_3 were then characterized by FTIR spec-

troscopy of adsorbed CO and NO. Following a reduction in hydrogen at 573 K, the room temperature adsorption of CO on W/γ-Al_2O_3 gave no significant IR bands while NO adsorption only shows weak bands at 1554 cm^{-1} and 1235 cm^{-1} that are attributed to nitrite and nitrate species on the alumina support. Surface science studies [6,13] have shown that NO adsorbs dissociatively on W at room temperature. In addition Yan et al. [14] have demonstrated that W/γ-Al_2O_3 catalysts reduced at high temperature (> 773 K) exposed W^{5+} and W^{+4} sites that are able to absorb CO and NO. Kazusaka and Howe [8] performed an IR study of adsorbed NO on W/γ-Al_2O_3 prepared from $W(CO)_6$. Samples were prepared in situ to maintain a low valence state of W. In this way they were able to observe bands at 1795 cm^{-1} and 1685 cm^{-1} that were assigned to dinitrosyl species adsorbed on W^{4+}. Taking into account the preparation method used in the present study we also expected to obtain partially reduced W on γ-Al_2O_3 catalysts, but the low metal content and the inevitable exposure to ambient air during sample handling for the FTIR experiments may lead to W oxidation.

Fig. 3 displays the spectra of CO adsorption on reduced Pd/γ-Al_2O_3 and Pd–W/γ-Al_2O_3
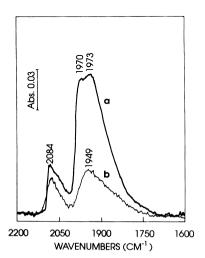

Fig. 4. FTIR Spectra of NO adsorbed on Pd/γ-Al_2O_3 (a) and Pd–W/γ-Al_2O_3 (b)

catalysts. On Pd/γ-Al_2O_3, typical bands assigned to linear (2084 cm^{-1}) and bridge species (1937–1970 cm^{-1}) can be recognized. The predominance of bridged CO indicates that the Pd sample had a moderate metal dispersion. Upon W addition, a strong attenuation on the CO band intensities was observed, a clear evidence that W was being deposited on the Pd particles; the main attenuation was observed for multicoordinated CO. As the decrease in band intensity was not accompanied by a shift in frequency, we conclude that the addition of W does not lead to a dilution of the surface Pd atoms or indicate the presence of electronic effects. The suppression of CO chemisorption demonstrates that the method of preparation has been successful to obtain W in close contact with Pd. IR bands due to CO adsorbed on partially reduced W, as reported by Yan et al. [14], were not observed. However it is important to note that our experiments were carried out with low loaded samples exposed to much lower NO pressures.

Fig. 4 illustrates the infrared spectra for NO adsorption on Pd/γ-Al_2O_3 and Pd–W/γ-Al_2O_3. On Pd/γ-Al_2O_3 the sharp peak located at 1732 cm^{-1} is assigned to linear NO on Pd

Fig. 3. FTIR Spectra of CO adsorbed on Pd/γ-Al_2O_3 (a) and Pd–W/γ-Al_2O_3 (b)

[15,16]. In addition there is a low intensity signal at 1650 cm^{-1} attributed to bridged NO. In the low frequency region, only the band at 1232 cm^{-1}, which was also observed on W/γ-Al$_2$O$_3$, is revealed.

When NO was added to Pd–W/γ-Al$_2$O$_3$ the band at 1732 cm^{-1} was absent but more relevant features, associated to nitrite and nitrate species, appeared below 1600 cm^{-1}. The 1232 cm^{-1} band, identical to that observed on W/γ-Al$_2$O$_3$ and Pd/γ-Al$_2$O$_3$, has been previously assigned to bridge nitrite species on γ-Al$_2$O$_3$ [17,18]. Additional bands can be seen at 1315 cm^{-1}, 1470 cm^{-1} and 1560 cm^{-1}. The one at 1470 cm^{-1} is tentatively assigned to a linearly coordinated nitrite ion [18]. Those that are broad and intense, at 1315 cm^{-1} and 1560 cm^{-1}, have been ascribed to nitrate species [17,18]. First it is important to state that these bands cannot be removed by evacuation or heating. Since they were not observed when Pd/γ-Al$_2$O$_3$ or W/γ-Al$_2$O$_3$ were exposed to NO, the results indicate a promotional effect due to both Pd and W. If the Pd particles are covered to a certain extent by W, the close proximity of both metals facilitates the partial reduction of W during the hydrogen treatment at 573 K. We suspect that these Pd–W particles induce the dissociation of NO. Probably some oxygen atoms lead to W oxidation while others remain on the Pd surface and react with NO to form NO$_2$, which in turn could be responsible for the strong nitrate bands found on γ-Al$_2$O$_3$.

This interpretation is in accordance with recent results. Hoost et al. [16] have shown that adsorption of NO on oxidized Pd/γ-Al$_2$O$_3$ enhanced the bands due to nitrite and nitrate species, suggesting the possibility of NO oxidation. Another relevant study is that of Centi et al. [19]; they found that NO adsorption on γ-Al$_2$O$_3$, at 300°C, revealed bands quite similar to those shown in Fig. 4. Consequently the results of the FTIR study also suggest that the preparation of Pd–W/γ-Al$_2$O$_3$, using a modified hexacarbonyl precursor, leads to a specific Pd–W interaction and to sites that modify the

chemisorption of NO relative to that observed on Pd/γ-Al$_2$O$_3$ and W/γ-Al$_2$O$_3$.
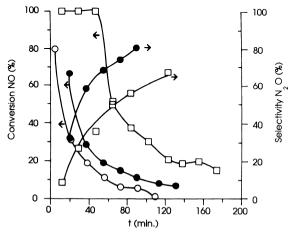
3.3. NO decomposition

In order to determine if the NO (Pd–W) interaction mentioned above plays a beneficial role in the NO decomposition reaction, the catalytic activity and selectivity of all samples have been examined at 473 K.

Fig. 5 shows that Pd/γ-Al$_2$O$_3$ and W/γ-Al$_2$O$_3$ catalysts exhibit a comparable behaviour as a function of time. The initial activity was very high but it was followed by a deactivation period of about 100 min. It can be seen that the W/γ-Al$_2$O$_3$ sample is slightly more active. On the other hand the behaviour of Pd–W/γ-Al$_2$O$_3$ was quite different; it showed 100% conversion of NO for at least 80 min and then deactivates like the other samples. This enhanced activity is attributed to a close Pd–W interaction; it should be observed that the behaviour of Pd–W/γ-Al$_2$O$_3$ cannot be predicted from the combined effect of Pd/γ-Al$_2$O$_3$ and W/γ-Al$_2$O$_3$.

It is generally accepted that the catalytic decomposition of NO occurs on reduced metals [20]. The reaction mechanism involves the adsorption of NO on the metal surface followed by dissociation into nitrogen and oxygen, and

Fig. 5. Activity and selectivity for NO decomposition at 473 K: ○ Pd/γ-Al$_2$O$_3$; ● W/γ-Al$_2$O$_3$; □ Pd–W/γ-Al$_2$O$_3$. For clarity the selectivity of Pd/γ-Al$_2$O$_3$ has been omitted.

the recombination of adsorbed nitrogen atoms to form N_2. However the oxygen produced remains strongly adsorbed, inhibiting further adsorption of NO and consequently the catalysts deactivate. Depending on the reaction conditions the tightly bound oxygen may even lead to oxidation of the metal. Another important reaction pathway on metal surfaces is that of adsorbed NO with adsorbed nitrogen atoms to form N_2O. However the essential role of the catalyst surface is the dissociation of NO. Evidence for molecular adsorption of NO on Pd has been provided by FTIR studies [15,16] and confirmed here. On the other hand the dissociation of chemisorbed NO to form N_2 and N_2O on Pd has been demonstrated by TPD experiments. Because oxygen desorption is not observed the formation of subsurface oxygen and even dissolution of oxygen into the bulk was suggested [21,22].

The method of preparation described above leads to partially reduced W atoms that are close to Pd° sites and this interaction facilitates the fixation of oxygen and becomes responsible for the period of high activity observed on the $Pd–W/\gamma\text{-}Al_2O_3$ catalysts. However it is important to emphasize that W deposited on the Al_2O_3 surface exhibits a high initial activity by itself, and this is a clear indication of the existence of partially reduced species even in the absence of Pd. Evolution of O_2 was never detected which suggests that this decomposition product is in fact retained in the catalysts surface or leads to metal oxidation.

At high conversion values the main nitrogen containing product for all samples was N_2; the formation of N_2O was observed to increase along with catalyst deactivation. The N_2 mass balance based on the amounts of N_2O and N_2 formed, and unreacted NO, gave approximate results, due to the low NO content in the feed mixture and the inevitable chromatographic errors. Consequently we cannot discard the formation of small amounts of NO_2, from NO oxidation, and then of nitrite or nitrate species on the alumina surface.

These results confirm the conclusion of the FTIR study in the sense that the preparation of $Pd–W/\gamma\text{-}Al_2O_3$ by reaction of modified tungsten hexacarbonyl with $Pd/\gamma\text{-}Al_2O_3$, leads to a Pd–W interaction that stabilizes W in a partially reduced state. Moreover the catalytic behaviour of the $W/\gamma\text{-}Al_2O_3$ also indicates the existence of partially reduced W species on the alumina support. Consequently the preparation method described above offers a convenient route to obtain bimetallic catalysts with metal–metal interactions. Although supported Pt–Mo and Pt–W catalysts with a proven metal–metal interaction have already been prepared using organometallic precursors [20,23] the present study is the first to consider the reactivity of a reduced metal surface with hexacarbonyl compounds. The preparation method has been successful to control the oxidation state of W but the inconvenience of using PPh_3 ligands is the insertion of P. In addition the decrease in surface acidity may have an adverse effect for NO_x reduction with hydrocarbons. A recent publication [24] emphasizes the beneficial role of WO_3 to increase the acidity and the catalytic activity of $\gamma\text{-}Al_2O_3$ for NO_x reduction. We are planning to address this subject in a future study.

4. Conclusions

It has been demonstrated that the photochemical reaction of W hexacarbonyl with PPh_3 in the presence of $Pd/\gamma\text{-}Al_2O_3$ allows the adsorption of mono and disubstituted carbonyl species on the palladium–alumina surfaces. The $Pd–W/\gamma\text{-}Al_2O_3$ catalyst obtained after thermal decomposition and reduction stabilizes W in a partially reduced state that, to a certain extent, is in close association with the Pd atoms. FTIR analysis of adsorbed NH_3 demonstrated that the method of preparation practically suppresses the Lewis acidity of the alumina support. In addition FTIR studies have shown that the resulting Pd–W interaction modifies the chemisorptive properties for NO adsorption with respect to

those of the monometallic Pd and W catalysts. Consequently the bimetallic catalyst exhibits an enhanced activity for NO decomposition.

Acknowledgements

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